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with an without the magnetic field. The fact that the rates differed in the experiment indicates that in the strong flux regime, the theory presented here must be modified.

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Absorption from Neutral Acceptors in GaAs and GaP

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We present a new calculation of the absorption due to transitions of holes between neutral acceptors and the various valence-band sublevels in GaAs and GaP. The acceptor wave function was approximated by a previously suggested expression for ground-state wave functions appropriate to complicated band extrema. Numerical calculations of the absorption from inter-valence-band transitions of free holes and neutral acceptors have been performed. Good agreement with experimental results is obtained.

I. INTRODUCTION

Optical transitions of free holes between pairs of the three sublevels of the valence band in GaAs and GaP give rise to a characteristic infrared absorption.[1-3] In GaAs at room temperature, the absorption has qualitatively the same shape as the absorption due to the same transitions among the valence-band levels of Ge.[2,4-7] Balslev[2] calculated the room-temperature absorption in p-type GaAs and obtained good agreement with experimental results. No interpretation of the absorption at 77 °K[1] has been published. Recently, Wiley and DiDomenico (WD)[3] measured the infrared absorption of p-type GaP. In contrast to GaAs, the absorption spectrum of GaP has no significant structure. WD made a calculation of the room-temperature absorption, based on the model of Kahn[4] for inter-valence-band transitions. To get agreement with experimental results it was necessary to use two adjustable parameters plus a contribution from intraband free-carrier absorption. At 90 °K, WD identified the absorption as being due to neutral acceptors. No calculation of this absorption was made.

In this work, we present a model for absorption from neutral acceptors with applications to GaAs and GaP. The basic absorption mechanism is that of transitions of holes from the acceptor state to the sublevels of the valence band. In Sec. II we develop the necessary theory for absorption due to such transitions. Analytical calculations based on a simple band structure are performed and a comparison is made with the absorption from inter-valence-band transitions of free holes. In order to perform numerical calculations on GaAs and GaP we make approximations for the acceptor wave function. Here, we use a previously analyzed form for the ground-state wave function.[8] In Sec. III we give a description of the computation of the absorption in a model[2,7] which takes into account the detailed structure of the valence band and the optical matrix elements. In Sec. IV we present experimental results for the absorption of p-type GaAs together with the experimental results of WD for p-type GaP. The experimental data are compared with computed spectra for inter-valence-band absorption and for absorption from neutral acceptors.

II. ABSORPTION FROM NEUTRAL ACCEPTORS

A. Theory

At a sufficiently low temperature, the free holes in a semiconductor return to the acceptor ions and then neutralize these negatively charged states. The hole is in other words bound to the negative acceptor center. Let the valence-band Bloch functions with wave vector $\vec{k}$ be given by $\phi_{i,\vec{k}}(\vec{r}) = u_{i\vec{k}}(\vec{r})e^{i\vec{k}\cdot\vec{r}}$, where $i = 1$, 2, and 3 denote the heavy-hole band, light-hole band, and spin-orbit split-off band, respectively. $u_{i,\vec{k}}(\vec{r})$ are periodic func-

tions of position $\vec{r}$ with the periodicity of the lattice. The wave function $\psi(\vec{r})$ of the bound hole can be expanded in terms of the Bloch functions of the valence bands around $\vec{k}=0$:

$$\psi(\vec{r})=\sum_{i,\vec{k}} a_i(\vec{k})\phi_{i,\vec{k}}(\vec{r}), \tag{1}$$

where the summation extends over all quantum states $\vec{k}$. We shall here only be concerned with the case where all the carriers occupy the acceptor ground state of energy E_a.

The physical absorption mechanism consists of optical excitation of bound holes to free-carrier states in the valence-band levels. Let index a denote the acceptor state. The optical matrix element for a transition from the acceptor state to a free-hole state at wave vector $\vec{k}$ in valence band j is given by

$$M_{aj}(\vec{k})=\langle \phi_{j,\vec{k}}(\vec{r})\,|\,\vec{e}\cdot\vec{p}\,|\,\psi(\vec{r})\rangle, \tag{2}$$

where $\vec{e}$ is a unit vector in the direction of the polarization of the incident light. The absorption constant due to transitions to band j is then[9]

$$\alpha_{aj}=(N_a/n)(C/\hbar\omega)\int d^3\vec{k}\,|M_{aj}|^2(f_a-f_j) \times\delta(E_a-\epsilon_j(\vec{k})-\hbar\omega), \tag{3}$$

where N_a is the concentration of neutral acceptors, C a constant, and n is the refractive index. f_a and f_j are normalized occupation probabilities for holes with energies E_a and $\epsilon_j(\vec{k})$, respectively. At the low temperatures of interest here $f_a\simeq 1$ and $f_j\simeq 0$. Inserting the expression (1) the matrix element (2) can be written

$$M_{aj}=\sum_i a_i(\vec{k})M_{ij}(\vec{k}) \quad . \tag{4}$$

M_{ij} is the optical matrix element[4,14] for transitions between the valence band levels i and j,

$$M_{ij}(\vec{k})=\langle\phi_{j,\vec{k}}(\vec{r})\,|\,\vec{e}\cdot\vec{p}\,|\,\phi_{i,\vec{k}}(\vec{r})\rangle. \tag{5}$$

Using Eq. (4) the expression (3) for α_{aj} can be written

$$\alpha_{aj}=(N_a/n)(C/\hbar\omega)\int d^3\vec{k}\,|\textstyle\sum_i a_i(\vec{k})M_{ij}|^2 \times\delta(E_a-\epsilon_j(\vec{k})-\hbar\omega). \tag{6}$$

It is useful to compare this expression with the absorption arising from transitions of free holes[2,4,7,14] of concentration p between bands i and j:

$$\alpha_{ij}=(pC/n\hbar\omega)\int d^3\vec{k}\,|M_{ij}|^2(f_i-f_j)\delta(\epsilon_i(\vec{k})-\epsilon_j(\vec{k})-\hbar\omega), \tag{7}$$

where for nondegenerate statistics at temperature T, $f_i\propto(k_BT)^{-3/2}e^{\epsilon_i(\vec{k})/k_BT}$ $[\epsilon_i(\vec{k})\lesssim 0]$. Here, k_B is Boltzmann's constant. In Eq. (6) normalization of the wave function (1) requires $\sum_{i,\vec{k}}|a_i(\vec{k})|^2=1$, which in Eq. (7) is replaced by $\sum_{i,\vec{k}}f_i(\epsilon_i(\vec{k}))=1$.

The absorption due to transitions from a localized state to free-carrier states in the valence bands has then been broken up into a sum over momentum-conserving transitions between the valence-band levels. The absorption from neutral acceptors is then expressed by the same quantities as determine the inter-valence-band absorption, the thermal occupation probability f_i in Eq. (7) essentially being replaced by the probability amplitude $|a_i|^2$ in Eq. (6). α_{ij} and α_{aj} can, therefore, be computed numerically by the same procedure. This is particularly convenient since the computation of inter-valence-band absorption can be performed by very accurate methods.[2,7]

B. Model Based on Simple Band Structure

In order to investigate the main features of the absorption from neutral acceptors, we shall assume spherical heavy-hole and split-off bands of masses m_1 and m_3, respectively. The $\vec{k}=0$ separation between these bands is Δ, the spin-orbit splitting, which is assumed much larger than the acceptor binding energy. We furthermore assume that the light-hole mass is much smaller than the heavy-hole mass. The coupling between the acceptor state and the split-off and light-hole bands will then be neglected such that

$$\psi(\vec{r})\simeq\textstyle\sum_{\vec{k}} a_1(\vec{k})\,\phi_{1,\vec{k}}(\vec{r}).$$

For a hydrogenic ground state $a_1(\vec{k})$ is the Fourier transform of the ground-state hydrogenlike wave function[10]:

$$a_1(\vec{k})=8\sqrt{\pi}\,\lambda^{5/2}/(\lambda^2+k^2)^2 \quad , \tag{8}$$

where $\lambda=1/a_H$, a_H being the Bohr radius of the problem. The acceptor binding energy is given by $E_a=(\hbar^2/2m_1)\lambda^2$, and Eq. (8) can then be written

$$a_1(\vec{k})\propto[E_a-\epsilon_1(\vec{k})]^{-2}. \tag{9}$$

At photon energies larger than the spin-orbit splitting, the main part of the absorption is due to optical excitation of carriers in the acceptor state to the split-off band, a-3 transitions. Using $^4|M_{ij}|^2\propto k^2$ together with the above-mentioned approximation, we find

$$\alpha_{a3}=K\frac{16}{\pi}\frac{N_a}{n\hbar\omega}(E_a)^{-3/2}[\hbar\omega-(\Delta+E_a)]^{3/2} \times\left(1+\frac{m_1}{m_3}\frac{\hbar\omega-(\Delta+E_a)}{E_a}\right)^{-4}, \tag{10}$$

where K is a constant. The corresponding expression for 1-3 transitions of free holes is given by Kahn[4]:

$$\alpha_{13}=K\frac{2}{\sqrt{\pi}}\frac{p}{n\hbar\omega}(k_BT)^{-3/2}(\hbar\omega-\Delta)^{3/2} \times\exp\left(-\frac{m_3}{m_1-m_3}\frac{\hbar\omega-\Delta}{k_BT}\right). \tag{11}$$

In these expressions, the increase of absorption close to $\hbar\omega\simeq\Delta$ is due to the influence of density of states and optical matrix elements. The behavior

at high photon energies is dominated by the probability amplitude $|a_1|^2$ for α_{a3} and by the thermal occupation probability for α_{13}. The threshold energy for a-3 transitions is $\Delta + E_a$ compared to Δ for 1-3 transitions.

The maximum of the absorption occurs at photon energies of

$$\hbar\omega_{13}^{\max} \simeq \Delta + \tfrac{3}{2}k_B T[(m_1 - m_3)/m_3],$$
$$\hbar\omega_{a3}^{\max} \simeq \Delta + E_a[1 + \tfrac{3}{5}(m_1/m_3)]. \quad (12)$$

For $N_a = p$ the ratios between the maximum absorption cross sections is

$$\alpha_{a3}^{\max}/\alpha_{13}^{\max} \simeq 0.80 \times [m_1/(m_1 - m_3)]^{3/2}. \quad (13)$$

In most materials, the ratio $\alpha_{a3}^{\max}/\alpha_{13}^{\max}$ is larger than unity. (GaAs : 1.20; GaP : 1.40). The maximum absorption will then increase for decreasing temperatures where more holes are bound to acceptor sites.

Within this simple theory, the absorption from neutral acceptors thus provides information about the acceptor binding energy from the position of the maximum absorption [Eq. (12)]. Owing to the one-to-one correspondence between photon energy and wave vector the acceptor wave function, given by $a_1(\vec{k})$, can be found.

C. Approximations for GaAs and GaP

The actual valence-band structure of GaAs and GaP is complicated by warping and by nonparabolicity. We shall first consider the problem of determining the Fourier components $a_1(\vec{k})$ and $a_2(\vec{k})$ of the bound-hole wave function (1). For a carrier with complicated effective mass bound by a Coulomb potential, we have previously[8] suggested the approximate wave function

$$a_i(\vec{k}) = Q_i[E_a - \epsilon_i(\vec{k})]^{-q}[E_a - \epsilon(\vec{k})]^{q-2} \quad , \quad (14)$$

where Q_i is a normalization constant, $\epsilon_i(\vec{k}) = -\hbar^2 k^2/2m_i$, m_i being the average $\vec{k} = 0$ mass of band i. E_a is the actual experimental value of the acceptor binding energy. Q_i are normalization constants to be discussed in connection with the actual band structure and q is an anisotropy parameter. This result was derived from an iterative procedure, based on the effective-mass equation in the momentum representation. For a band with energy given by $\epsilon(\vec{k})$ $[\epsilon(\vec{k}) < 0]$ this equation is [8,11]

$$[\epsilon(\vec{k}) - E_a]a(\vec{k}) + \int d^3\vec{k}'\, a(\vec{k}')U(\vec{k} - \vec{k}'), \quad (15)$$

where $U(\vec{k})$ is the Fourier transform of the impurity potential. The form (15) is very suitable for iterative methods since a trial function $a^0(\vec{k})$ inserted in the integral produces a new function

$$a^1(\vec{k}) = \frac{1}{E_a - \epsilon(\vec{k})} \int d^3\vec{k}'\, a^0(\vec{k}')U(\vec{k} - \vec{k}') \quad , \quad (16)$$

which is better than $a^0(\vec{k})$. In Eq. (14), $q = 2$ is the zero-order trial function, obtained from the case of spherical bands [Eq. (9)]. The first iteration yields the wave function with $q = 1$. The formula (14) was examined[8] for ellipsoidal, parabolic bands and for nonparabolic, isotropic bands in the range $0 \leq q \leq 1$. The best result for the expectation value of the ground-state energy was obtained for $q \simeq 0.5$.

Figures 1 and 2 show the valence-band structure of GaAs and GaP as calculated from the four-band $\vec{k} \cdot \vec{p}$ model described in Sec. III. The parabolic behavior of the heavy-hole bands is only present in the ⟨100⟩ and ⟨111⟩ directions. In other directions, small deviations from parabolicity occur. The average $\vec{k} = 0$ masses are displayed in Table I. The coupling from the acceptor to the valence bands is dependent on the hole energy compared to the acceptor energy. Owing to the energy denominator in Eq. (14) we shall neglect the admixture of split-off band states in the acceptor wave function (1). For GaAs, the light-hole band can be considered as a remote band except in the region close to $\vec{k} = 0$. This region contributes, however, little to the absorption since the optical matrix elements depend on the square of the wave vector. The contribution from light-hole states in Eq. (1) will therefore be neglected. The matrix elements of Eq. (4) are in this approximation

$$M_{a1} \simeq a_1 M_{11}, \quad M_{a2} \simeq a_1 M_{12}, \quad M_{a3} \simeq a_1 M_{13}, \quad (17)$$

with

$$\sum_{\vec{k}} |a_1(\vec{k})|^2 = 1 \quad .$$

For GaP the heavy- and light-hole band are

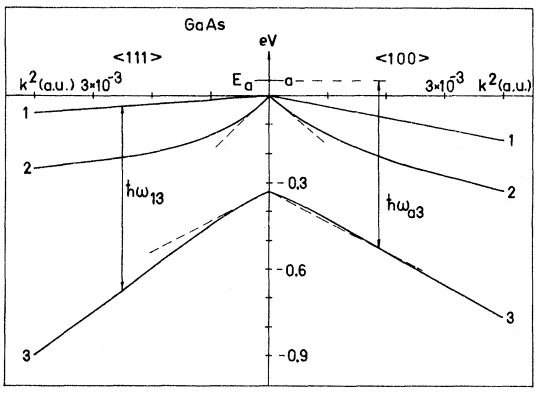

FIG. 1. Valence-band structure of GaAs at 300 °K in the ⟨100⟩ and ⟨111⟩ directions (1 a.u. $= 1/a_0$). Full line: calculated by the four-band $\vec{k} \cdot \vec{p}$ model described in Sec. III. Broken line: $\vec{k} = 0$ slopes. Left-hand side illustrates 1-3 transitions. Right-hand side illustrates transitions of bound holes from the acceptor level to the split-off band.

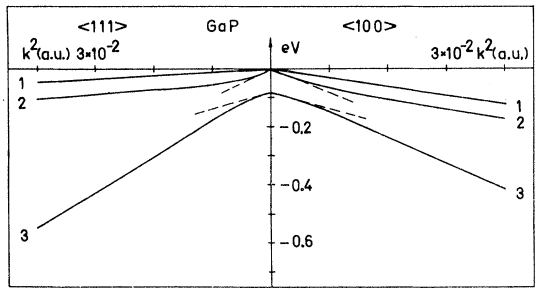

FIG. 2. Valence-band structure of GaP in the ⟨100⟩ and ⟨111⟩ directions. Full line: calculated from four-band $\vec{k}\cdot\vec{p}$ model. Broken line: $\vec{k}=0$ slopes.

parallel over most of the region in $\vec{k}$ space which contributes significantly to the absorption. The asymptotic distance between the bands is $\frac{2}{3}\Delta = 55$ meV. This distance can over a large part of $\vec{k}$ space be considered as small compared to the energy separation between the acceptor state and the two bands. Asymptotically, we must thus have $|a_1| = |a_2|$ yielding $|Q_1| \simeq |Q_2|$ at large wave vectors. We are not able to determine the phase of a_1 and a_2 and in Eq. (6) we must, therefore, make the approximation

$$|\textstyle\sum_i a_i M_{ij}|^2 \simeq \sum_i |a_i|^2 |M_{ij}|^2 \quad .$$

The matrix elements M_{aj} in Eq. (4) are thus given by

$$\begin{aligned} |M_{a1}|^2 &= |a_1|^2|M_{11}|^2 + |a_2|^2|M_{12}|^2 \quad , \\ |M_{a2}|^2 &= |a_1|^2|M_{21}|^2 + |a_2|^2|M_{22}|^2 \quad , \\ |M_{a3}|^2 &= |a_1|^2|M_{13}|^2 + |a_2|^2|M_{23}|^2 \quad , \end{aligned} \tag{18}$$

with

$$\textstyle\sum_{\vec{k}} |a_1|^2 + |a_2|^2 = 1 \quad .$$

III. COMPUTATION OF ABSORPTION CONSTANT

A procedure for numerical computation of the absorption constant has been set up. Except for minor details, the calculation was performed as described by Arthus, Baynham, Fawcett, and Paige[7] for the absorption from inter-valence-band transitions in Ge. In our $\vec{k}\cdot\vec{p}$ treatment of the energy levels, we have taken into account the twofold-degenerate Kramers doublets of the three Γ_{15} valence-band levels and the $\vec{k}=0$ conduction-band state Γ_1. The energies of these states were found by diagonalizing 8×8 Hermitian matrices. The $\vec{k}\cdot\vec{p}$-matrix elements were the k linear terms between the valence bands and the conduction band[12] and k^2 elements[13,14] giving the interaction between the valence-band levels through intermediate states, except the $\vec{k}=0$ conduction-band level. Our $\vec{k}\cdot\vec{p}$ model is similar to the one used by Balslev[2] but no approximations were made in the present calculation. The absorption spectrum was obtained in the form of a histogram. A Gaussian broadening[15] was applied to the histogram. The standard deviation of the broadening was 10 meV at 77 and 90 °K and 15 meV at 300 °K. The fluctuations in the absorption spectrum thus obtained were typically 5%. The absorption from free holes was calculated by taking into account all kinds of inter-valence-band transitions, i.e., 1-2, 2-3, and 1-3 transitions. In the calculation of the absorption from bound holes, Eq. (6) was used with the approximations for the matrix elements discussed in Sec. IIC.

Calculations were performed for GaAs both with the experimentally determined valence-band parameters of Balslev[2] and with the calculated ones of Lawaetz.[16] The latter gave 10% larger absorption cross section than the former but apart from this, no deviations were found. In the calculation on GaP, the valence-band parameters of Lawaetz[16] were used. Except for the acceptor binding energy and the anisotropy parameter q, no adjustable parameters were used. The latter was varied in the interval $0 \leq q \leq 1$, which only produced a rather small effect. It should be noted that the absolute value of the absorption constant was calculated. The parameters used in the calculation are displayed in Table I.

IV. COMPARISON WITH EXPERIMENT

A. Results on GaAs

Absorption measurements were carried out on Zn-doped GaAs at 300 and 77 °K. The absorption was determined from sample-in–sample-out measurements, using a refractive index of 3.3. The concentration of free carriers determined from Hall measurements was 1.4×10^{17} cm^{-3} at 300 °K and 3.0×10^{16} cm^{-3} at 77 °K. The concentration of uncompensated acceptors is equal to the carrier concentration at 300 °K. The measured

TABLE I. Valence-band parameters (Ref. 16) of GaAs and GaP.

Parameter	GaAs	GaP	Unit
A	−7.65	−4.20	$\hbar/2m_0$
B	−4.82	−1.96	···
N	−19.68	−9.96	···
P^2	25.7	22.2	(eV)$\hbar^2/2m_0$
$\langle m_1\rangle$	0.62	0.79	m_0
$\langle m_2\rangle$	0.074	0.14	···
$\langle m_3\rangle$	0.15	0.24	···
$E_{0,300\,°K}$	1.43[a]	2.78[b]	eV
$E_{0,77\,°K}$	1.52[a]	2.86[b]	···
Δ	0.33[c]	0.082[b]	···

[a]M. P. Sturge, Phys. Rev. 127, 768 (1963).
[b]P. J. Dean, G. Kaminsky, and R. B. Zetterstrom, J. Appl. Phys. 38, 3551 (1967).
[c]Reference 1.

absorption at room temperature is shown in Fig. 3 together with the calculated absorption from inter-valence-band transitions of free carriers at this temperature. A constant contribution of 1 cm^{-1} has been subtracted from all experimental values. Apart from this correction, no adjustable parameters were used. There is excellent agreement between theory and experiment at large photon energies. For $\hbar\omega < 0.45$ eV, there is a significant additional absorption. The experimental absorption cross section at 0.42 eV is 1.3×10^{-16} cm^2. Braunstein[1] found values between 0.65 and 0.9×10^{-16} cm^2. The calculated cross section at 0.45 eV is 1.1×10^{-16} cm^2 in agreement with Balslev's[2] result. The room-temperature absorption provides a check on the parameters of the calculation.

In Fig. 4 we show experimental and calculated absorption spectra at 77 °K. The calculated absorption from momentum-conserving transitions of free carriers (3.0×10^{16} cm^{-3}) is seen to deviate much from the experimental results. Assuming absorption due to transitions of bound holes to the split-off band to be predominant, we can estimate the acceptor binding energy from Eq. (12). The interval of photon energy from the spin-orbit splitting to the maximum of absorption is $\simeq 60$ meV. With the average mass of Table I for the heavy-hole band and split-off band, Eq. (12) yields $E_a \simeq 18$ meV. This is in good agreement with recent values[17] for the binding energy of Zn acceptors.

The absorption from neutral acceptors of concentration 1.1×10^{17} cm^{-3} was computed using the approximations (17). The calculation was done for different values of the acceptor binding energy and the anisotropy parameter q of Eq. (14). As expected from Eq. (10) the absorption is strongly

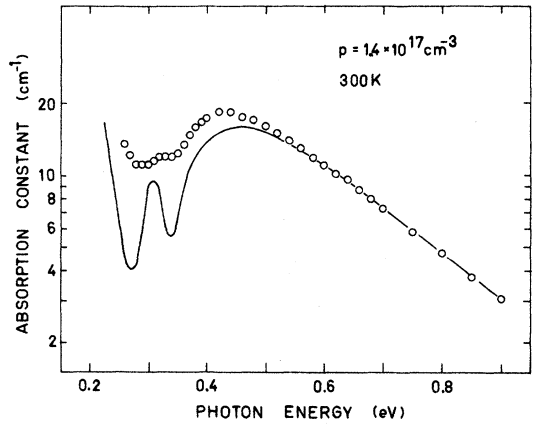

FIG. 3. Absorption constant of p-type GaAs at room temperature. Circles: experimental points. Full line: calculated spectrum from inter-valence-band transitions of free holes.

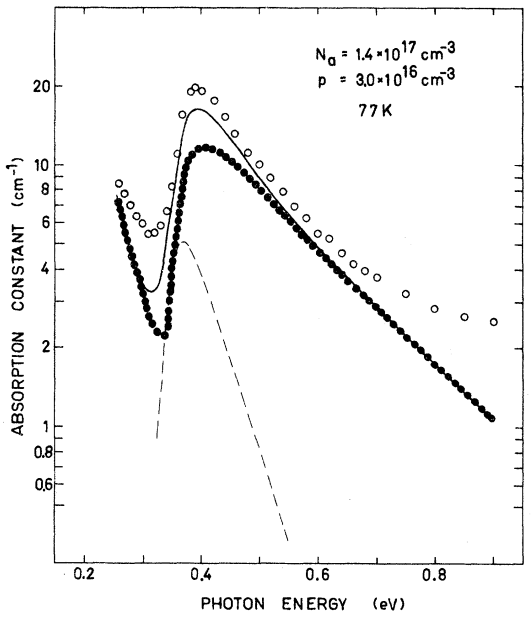

FIG. 4. Absorption constant of p-type GaAs at 77 °K. Open circles: experimental points. Broken line: calculated absorption from free-carrier transitions at 77 °K. Filled circles: calculated absorption from neutral acceptors ($E_a = 24$ meV, $q = 1$). Full line: calculated total contribution from free and bound holes.

dependent on E_a, the spectrum becoming broader with increasing binding energy. For given q, the acceptor binding energy which produced best agreement with experiment could be determined within 10%. The dependence of the absorption on q is rather weak. The best fit to experiment was obtained for $E_a = 24$ meV. A change of q from 0 to 1 produced a 20% larger absorption at $\hbar\omega = 0.90$ eV. The absorption has thus no significant dependence of q. The dotted line in Fig. 4 shows the calculated absorption from neutral acceptors with $E_a = 24$ meV, $q = 1$. The sum of the contributions from bound and free holes is seen to agree well with experimental data.

There is a disagreement between the experimental and calculated absorption around $\hbar\omega \simeq 0.30$ eV and for $\hbar\omega > 0.65$ eV. These regions correspond to transitions from the acceptor state to the light-hole band and split-off band, respectively (see Fig. 1). Neglecting the nonparabolicity of the split-off band, a transition from the acceptor state to this band with $\hbar\omega = 0.65$ eV takes place at $k \simeq 5\text{–}6\times10^{-2}$ a.u. (1 a.u. $= 1/a_0$). Transitions to the light-hole band at this wave vector correspond to photon energies from 0.25 to 0.32 eV. The reason for the disagreement is obviously that the strength of the Fourier coefficient $a_1(\vec{k})$ of Eq. (1) is underestimated at large wave vectors by the hydrogenlike wave function. A typical

spatial distance connected with $k = 6\times10^{-2}$ a.u. is $R = \frac{1}{2}\pi/(6\times10^{-2}$ a.u.$) \simeq 15$ Å. One would then expect the core potential of the Zn ion plus the local strain fields to extend that far out. For a deep acceptor level, Lucovsky[18] found that the excited acceptor states could be described by a long-range Coulombic potential. Accordingly, the core potential would be expected to reach out a distance between the first and second Bohr radius (10 and 40 Å) as found.

B. Results on GaP

For GaP, we have used the experimental results of WD[3] at 300 and 90 °K. As WD, we shall use wavelength scale instead of photon energy scale. Figure 5 shows the calculated absorption from free carriers at room temperature together with WD's experimental results for their sample B ($N_a = 2.0 \pm 0.2\times10^{17}$ cm^{-3}, $p = 1.6 \pm 0.2\times10^{17}$ cm^{-3} at 300 °K). The calculation was done with $p = 1.6 \times10^{17}$ cm^{-3}. As described by WD, the absorption bands from 1-3 and 2-3 transitions overlap. According to the band structure of Fig. 2, the region of 1-2 transitions occurs at wavelengths larger than $\simeq 24$ μ. Lattice absorption obscures the spectrum at $\lambda > 12$ μ. In the wavelength range of interest, 1-2 transitions, therefore, do not contribute to the absorption. The dashed line in Fig. 5 shows the contribution to the absorption from 2-3 transitions. This is most significant at large wavelenths and for $\lambda < 4$ μ, 2-3 transitions constitute only around 10% of the total absorption. The general agreement between calculated and experimental spectra is rather encouraging, the maximum deviation over the spectrum being 15%. We have not taken into account any contribution from neutral acceptors here since the uncertainty intervals for the acceptor and hole concentrations overlap. WD have shown that the free-carrier absorption of the heavy-hole band might be enhanced owing to the existence of intermediate states in the light-hole and split-off band. The deviation between our calculated spectrum and the measured absorption at long wavelengths is in good agreement with WD's estimate of the intraband free-carrier absorption.

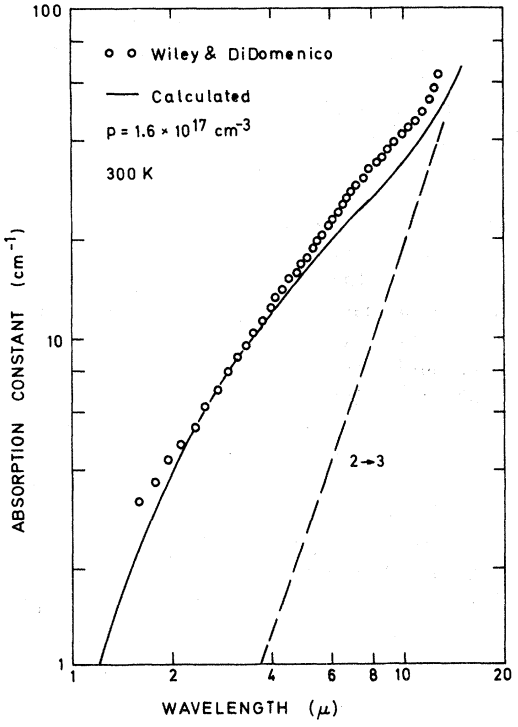

FIG. 5. Absorption constant of p-type GaP at room temperature. Circles: experimental results of Ref. 3. Full line: calculated absorption from free-carrier transitions. Broken line: contribution from 2-3 transitions.

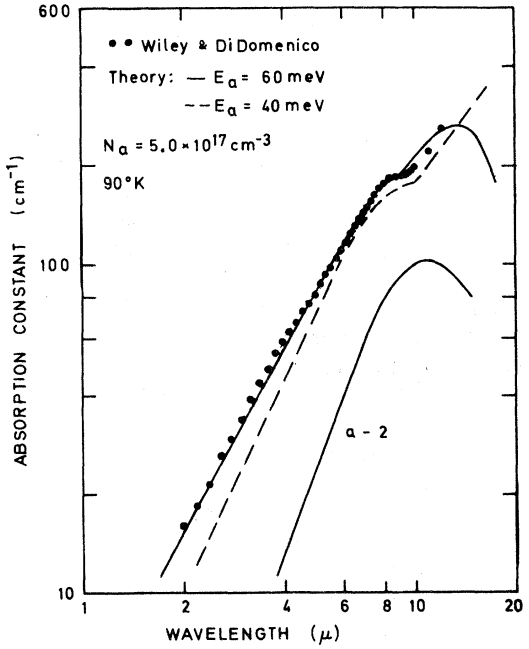

FIG. 6. Absorption constant of p-type GaP at 90 °K. Filled circles: experimental results of Ref. 3. Full line and broken line: calculated absorption from neutral acceptors with binding energies of 60 and 40 meV, respectively. Also shown separately is contribution from a-2 transitions ($E_a = 60$ meV). The value of the anisotropy parameter q is 1 in all calculations.

At 90 °K only a negligible fraction of free holes is present. The experimentally observed absorption at this temperature (Fig. 6) is therefore due to absorption from neutral acceptors. The absorption bands for transitions to the different sublevels of the valence band overlap (see Fig. 2). It is therefore not feasible to use the simple theory in Sec. II B. The numerical computations

of the absorption from neutral acceptors with the approximations of Eq. (18) gave best agreement with experimental data using $E_a = 60$ meV and $q = 1$. The experimentally determined binding energy of Zn acceptors in GaP is 60 meV at low concentrations.[19] Absorption spectra calculated with $q = 0$, $E_a = 60$ meV deviated 0–20% from the experimental values over the spectrum. This might, however, be due to the approximations of Eq. (18). The computed spectrum for $E_a = 60$ meV and $q = 1$ is shown in Fig. 6 together with the contribution from a-2 transitions. Also shown is the calculated absorption for $E_a = 40$ meV, $q = 1$. The general agreement with $E_a = 60$ meV, $q = 1$ is very good, both with respect to spectral shape and to absolute value.

Contrary to GaAs, there is no disagreement between experiment and theory at small wavelengths due to the influence of the core potential of the Zn ion and the local strain fields. The absorption at 2 μ corresponds to a-3 transitions at wave vector $k = 8 \times 10^{-2}$ a.u., corresponding approximately to spatial distances of 10 Å. The first and second Bohr radii are 5 and 20 Å, respectively, using the heavy-hole mass of Table I. As for GaAs, the spatial extension of the core potential is then within the second Bohr radius.

V. SUMMARY

In this work we have presented a theory which quantitatively accounts for the absorption from neutral acceptors in GaAs and GaP. This absorption is due to transitions of bound holes from the acceptor state to the valence-band sublevels. It can be calculated from the bound-hole wave function and the optical matrix elements between the valence-band levels. The parameters of the calculation have been checked by calculating the absorption due to inter-valence-band transitions. Here, good agreement with experimental results was obtained. In the calculation of absorption from neutral acceptors, the adjustable parameters were the acceptor binding energy E_a and the anisotropy parameter q. The values used for E_a are in good agreement with recent experimantal values. Only a weak dependence on q was observed.

The present model for absorption from neutral acceptors can be used in a study of acceptor wave functions. The bound-hole wave function is expanded in terms of Bloch functions of the valence-band levels. At any wave vector these expansion coefficients govern the absorption from transition of bound holes to all three valence-band levels. A computation of the absorption with a wave function slightly different from the actual one will therefore show disagreement with experiment in three regions of the spectrum (provided that all three regions are observable). As demonstrated for GaAs, this feature facilitates interpretation. We finally mention that whereas the inter-valence-band absorption can be partly superposed by absorption due to phonon-assisted processes, this effect should be small when all holes are frozen out.

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